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Process system engineering in biodiesel production: A review

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ABSTRACT

Biodiesel is fast becoming a popular alternative to fossil fuels, as it is natural, renewable and has low toxic emissions. Strategies that have been adopted to ensure continued growth of the biodiesel industry are policy development, reduction of biodiesel tax, offset funding for incremental fuel cost from CO_2 emission fuel and support for research and development of potential biodiesel feedstocks. Recent innovations of biodiesel processes are focused on the development of more efficient catalysts and in the utilization of novel reaction media such as supercritical fluids as well as on a variety of oil feedstocks such as virgin and waste oils. Biodiesel production involves complex processes which require systematic process design and optimization. The main aim of designing biodiesel plants is to maxime conversion of ethyl or methyl esters at the lowest capital cost of the plant. The design should also consider safety and environmental concerns. Process system engineering (PSE) is a systematic approach to design and analyze complex processes by using a variety of PSE tools for the optimization of biodiesel production. This paper reviews the latest PSE tools used in development of novel biodiesel processes. It describes the main PSE elements such as process model development and product design, simulation of biodiesel processes, optimization of biodiesel synthesis, and integration of reactor and separation systems. This review also highlights the sustainability of biodiesel production.

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1. Introduction

Fossil fuels remain as the main source of energy. Recent production of fossil fuels has reached up to 79% compared to other energy sources as shown in Fig. 1 [1]. However, the demand for fossil fuel as a primary energy source is exceeding its production, due to rising consumption of fossil fuel energy up to 83% in November 2010.

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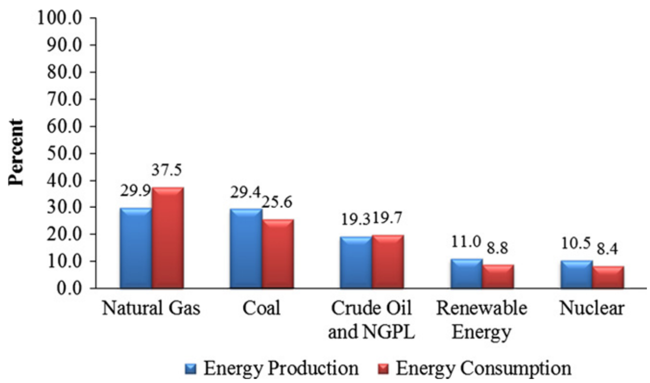


Fig. 1. World primary energy production and consumption in November 2010, per source.

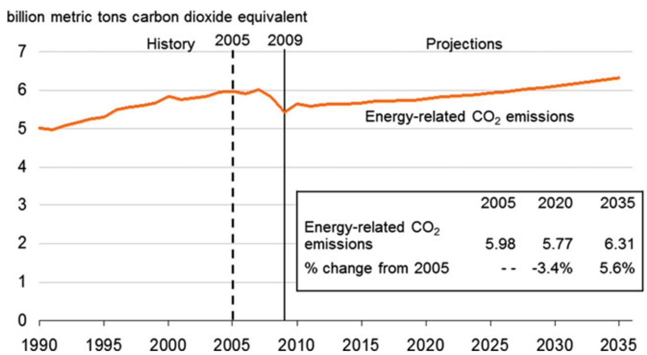


Fig. 2. U.S Energy-related carbon dioxide emissions from 1990 to 2035.

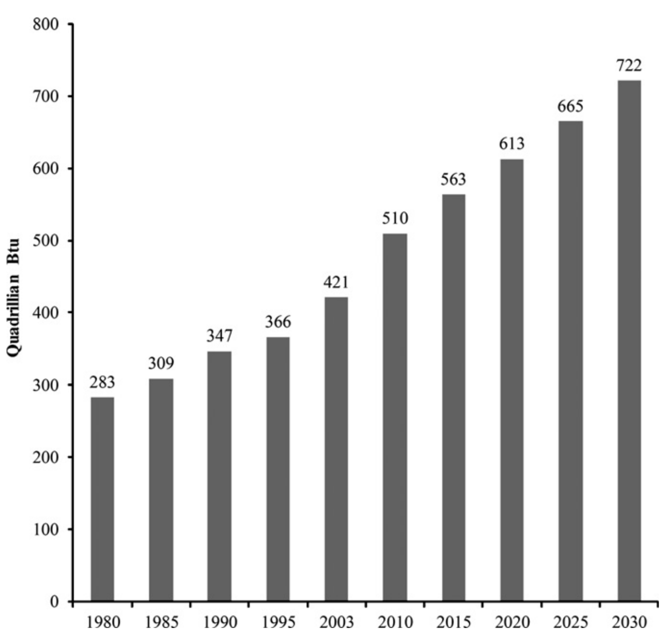


Fig. 3. World projections of energy consumption, 2003 to 2030.

Consumption of fossil fuel will cause adverse consequences especially to the natural environment. Combustion of fossil fuel increased the formation of carbon dioxide and by-products in the atmosphere and significantly caused the depletion of the ozone layer and increased global warming. This indicates that carbon and by-products emissions are directly proportional to energy consumption. The vulnerable ozone layers diminish in line with rapid industrial growth. As projected in Fig. 2, the energy related carbon dioxide emission shall continue to gradually rise until the year 2035 [2].

Energy consumption would certainly increase in the future in line with increasing population (Fig. 3) [2]. Thus, seeking alternatives to fossil fuels is vital. In addition to sustainable energy policy, renewable energy is an option to reduce dependencies on fossil fuels. Wind, hydro, solar, biomass, biofuel, geothermal and ocean energy are amongst the renewable energy resources that can help to supply energy for electrical power generation and transportation sectors. These natural power sources offer alternative means that can simultaneously save the environment and reduce reliance on fossil fuels.

Process system engineering (PSE) has long been recognized as a promising method to design and operate efficient and sustainable chemical process plants. It is a comprehensive, iterative and recursive problem solving process [3]. PSE offers solution to complex engineering system by enabling the use of viable tools and techniques to better manage and comprehend the complexity of the system. This article shall henceforth review every aspect of process system engineering such as model development, design, simulation and optimization as well as combinations of these elements that can be fruitfully used in improving the processes for biodiesel production.

2. Biodiesel production

Biodiesel is the most common biofuel used in Europe and internationally owing to its ready availability and renewability. Biodiesel is diesel fuel derived from natural and renewable sources for diesel engines that meet the specifications of ASTM D 6751. Biodiesel is produced from oils and fats, consisting of methyl or ethyl esters. Several methods have been employed to transform the oils and fats into biodiesel such as pyrolysis, microemulsion and transesterification. The transesterification reaction process of oils and fats is a common method used to produce biodiesel. It is often catalysed by either an acid, a base or an enzymatic catalyst. The process is a reversible reaction, as shown in Fig. 4 [4]. Excess amount of alcohol can help to accelerate the conversion of glycerides.

Biodiesel can be derived from various types of feedstock. Examples of biodiesel sources are: almond, andiroba (*Carapaguianensis*), babassu (*Orbignia* sp.), barley, camelina (Camelina *sativa*), coconut, copra, cumaru (*Dipteryxodorata*), *Cynaracardunculus*, fish oil, groundnut, Jatropha curcas, karanja (*Pongamiaglabra*), laurel, *Lesquerellafendleri, Madhucaindica*, microalgae (*Chlorella vulgaris*), oat, piqui (*Caryocar* sp.), poppy seed, rice, rubberseed, sesame, sorghum, tobacco seed, and wheat [5]. Among popular choice of vegetable oils for biodiesel are soybean oil [6], waste cooking oil [7], rapeseed oil [8], palm oil [9], sunflower oil [10]; and the canola, corn, olive and linseed oils.

Even though biodiesel can be derived from various types of feedstock, the production processes may differ depending on the properties of the oil. Biodiesel derived from feedstock with high fatty acids value normally require pre-treatment process called esterification before the transesterification reaction [11]. Thus, important properties of triglycerides for biodiesel preparation such as fatty acids value, saponification value and water content

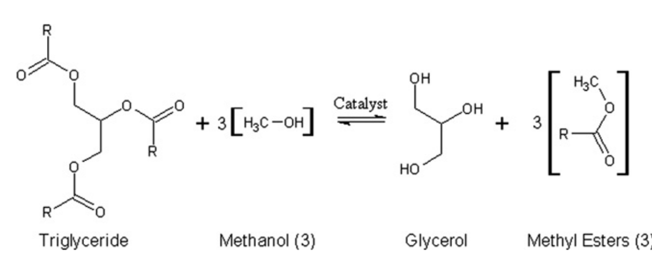


Fig. 4. Transesterification of triglycerides with alcohol.

need to be considered to determine the viable method of biodiesel production.

Other than that, if a crude oil is used as the feedstock, the oil is subjected to acid degumming process, and alkali refining; followed by the drying process before passing through the esterification and transesterification reaction.

Conventionally, the transesterification of triglycerides is conducted using homogeneous basic catalysts such as sodium hydroxide, sodium methoxide, potassium hydroxide, sodium amide, sodium hydride, potassium amide and potassium hydride [12–14]. Homogeneous acid-catalysed transesterification was much slower than alkali catalysis [15]. The acids could be sulphuric acid, phosphoric acid, hydrochloric acid or organic sulphonic acid. This type of catalyst is suitable to be used with low grade feedstock for biodiesel production such as waste cooking oil or Zanthoxylumbungeanum seed oil (ZSO) [16,17]. Applications of heterogeneous catalysts for biodiesel production have been reported recently [18].

The advantages of using heterogeneous base catalysts are that they are non-corrosive and easily separated from the liquid products. Alternatively, heterogeneous acid catalysts can be used in biodiesel production for oil containing high amount of free fatty acid. However, acid catalysts are hydrophilic and commonly possess slow reaction rate. Thus, the higher the reaction temperature, more pressure and longer reaction time are required [19]. Otherwise, the transesterification reaction can be catalysed by enzymes such as lipases, which are often favourable. Nozozyme 435, Candida rugosa, Rhizopusoryzae, Geotrichum sp. and Penicilliumexpansum lipase catalysts are among enzymatic catalysts that are used in biodiesel production [20,21].

Supercritical biodiesel production has recently gained researchers' interest as this new method was found to reduce transesterification time from several hours to several minutes without catalyst. The conversion of oil to methyl ester using the method was proven to be completed within three minutes, with the reaction rate about two orders of magnitude faster [22]. Supercritical biodiesel production requires high reaction temperature ranging from 200 to 550 °C, high pressure reaction and higher methanol to oil molar ratio compared to conventional biodiesel production. In catalysed transesterification, the presence of water should be avoided but under supercritical condition, the presence showed no negative effects to the methyl esters formation [23].

3. Model development for biodiesel production

3.1. Process model and product design

There are two possible approaches that may be used for the design of biodiesel process plant and integration. The first design approach begins with selecting a reactor and moving outward by adding a separation and recycle system. At each layer, decisions must be made according to the information available at that stage. This approach is based on heuristics or rules of thumb developed from the experience of the designer. Another approach for designing biodiesel process plant is by using a process superstructure. It starts by embedding all feasible process options and feasible interconnections as candidates for an optimal design structure. Redundant features are included to ensure that all features that could be part of optimal solutions are incorporated. Subsequently, any features considered infeasible are removed from the structure [24].

A complete design of biodiesel plant from waste cooking oil was conducted by Zhang et al. [25]. The biodiesel plant performance was assessed using alkali and acid catalysts. The processes in the production were esterification, transesterification, methanol recovery, water washing and FAME purification. Similar study was performed by Tapasvi et al. [26] but they incorporated the mass and energy balances in the process model. The model developed could be further applied in performing economic feasibility studies of biodiesel production. Soybean oil and canola oil were compared in terms of their process outputs. The processes of crude oil degumming, refining and drying were embedded before the transesterification reaction. Results showed that Canola oil had higher process outputs than soybean oil.

An integrated process model and product design of biodiesel manufacturing was employed by Chang and Liu [27]. Their research focused on the feed oil characterization, thermophysical property estimation, rigorous reaction kinetics, phase equilibrium for separation and purification units, and prediction of biodiesel fuel qualities. They employed alkali-catalysed transesterification process and predicted the reactor and separator performance, stream conditions and product qualities using various feedstocks. A further research on phase equilibrium systems for biodiesel production was conducted by Oliveira et al. [28] to determine the liquid-liquid equilibrium of multicomponent mixtures containing alcohols, glycerol, and fatty acid esters in the production and purification process. They employed cubic-plus-association equation of state to estimate binary interaction parameters. Other research that employs Peng–Robinson equation of state was by Tang et al. [29] to determine the methanol–triolein binary system at various temperatures and pressures.

In contrast to the aforementioned studies, Zong et al. [30] highlighted the lack of proven models and databanks for estimating thermo-physical properties of vegetable oil and blends. Hence, Zong et al. attempted the use of triglycerides pure component properties for modeling the biodiesel production processes. The method employed was fragment-based approach which comprised of constituent fragment-based modeling approach, identification of fragment-specific parameters, correlation of the parameters and estimation of double-bond effects. Subsequently, similar approach was employed for estimation of thermo physical properties for mono- and diglycerides [31]. As a result, the databank obtained managed to provide thermo-physical property for process modeling and design, simulation, and optimization of biodiesel production processes.

Design and operation of chemical plants by incorporating sustainability elements are currently desirable as it promoted minimum energy usage and wastes. Recent works showed that incorporation of sustainability elements into PSE approaches were capable of increasing profit of chemical plants. Halim and Srinivasan [32] employed combinations of different PSE approaches using simulation and optimization in the development of framework for generating sustainable design and operations alternatives. These initiatives for chemical process plants focused on waste minimization in the process plant. The methods used were knowledge-based simulation-optimization framework, and integration of heuristic-based waste diagnosis with process simulation and mathematical optimization.

Myint and El-Halwagi [33] conducted process analysis and optimization of biodiesel production from soybean oil through inter-connected activities such as process design and simulation. They carried out simulation studies on various separation configuration scenarios. The aim was to determine the interaction among the compounds; and separation behaviour of the compounds using different amounts of separating agents. For sustainable biodiesel plant, Myint and El-Halwagi had identified opportunities for process integration and cost minimization; and performed simulation with various mass and integration processes. They also conducted capital cost estimation, profitability

and sensitivity analyses. Similarly, Elms and El-Halwagi [34] also executed process design and optimization on biodiesel production and performed capital and operating cost estimation. However, they included the estimation of CO_2 emission in the biodiesel process design per effect of GHG policies. In short, the systematic approach for the design of biodiesel production processes per the GHG policies did provide a powerful decision-making tool for policy makers and producers.

3.2. Kinetics reaction modeling

Process model requires kinetics of reaction as it provides parameters useful to predict extent of the reaction at any time under particular conditions. Various kinetic studies have been conducted to describe the kinetics of biodiesel production using different catalysts and process conditions [9,35–39]. The kinetics data collected are normally dependent on predetermined factors such as types of reactor used, feedstock, and types of catalysts used, as well as reaction conditions such as reaction temperature and catalyst concentration. The reactions steps are shown in Eq. (1) where k1–8 is rate constants.

$$\begin{aligned} &\mathrm{TG}+\mathrm{CH_3OH} \underset{k_2}{\overset{k_1}{\Leftrightarrow}} \mathrm{DG}+R_1\mathrm{COOCH_3} \\ &\mathrm{DG}+\mathrm{CH_3OH} \underset{k_4}{\overset{k_3}{\Leftrightarrow}} \mathrm{MG}+R_2\mathrm{COOCH_3} \\ &\mathrm{MG}+\mathrm{CH_3OH} \underset{k_6}{\overset{k_5}{\Leftrightarrow}} \mathrm{GL}+R_3\mathrm{COOCH_3} \end{aligned} \tag{1}$$

Overall reaction:

$$\mathrm{TG}+3\mathrm{CH_3OH} \underset{k_8}{\overset{k_7}{\Leftrightarrow}} 3\mathrm{RCOOCH_3}+\mathrm{GL} \tag{2}$$

Mole balances:

$$\begin{aligned} &\mathrm{TG}: \frac{dC_{TG}}{dt} = -k_1C_{\mathrm{TG}}C_A + k_2C_{\mathrm{DG}}C_A - k_7C_{\mathrm{TG}}{C_A}^3 + k_8{C_{\mathrm{GL}}}^3C_A \\ &\mathrm{DG}: \frac{dC_{\mathrm{DG}}}{dt} = -k_3C_{\mathrm{DG}}C_A + k_4C_{\mathrm{MG}}C_E - k_2C_{\mathrm{DG}}C_E + k_1C_{\mathrm{TG}}C_A \\ &\mathrm{MG}: \frac{dC_{\mathrm{MG}}}{dt} = -k_4C_{\mathrm{MG}}C_E + k_3C_{\mathrm{DG}}C_A - k_5C_{\mathrm{MG}}C_A + k_6C_{\mathrm{GL}}C_E \\ &\mathrm{E}: \frac{dC_E}{dt} = k_1C_{\mathrm{TG}}C_A - k_2C_{\mathrm{DG}}C_E + k_3C_{\mathrm{DG}}C_A - k_4C_{\mathrm{MG}}C_E + k_5C_{\mathrm{MG}}C_A \\ &\qquad -k_6C_{\mathrm{GL}}C_E + k_7C_{\mathrm{TG}}{C_A}^3 - k_8C_{\mathrm{GL}}{C_E}^3 \\ &\mathrm{A}: \frac{dC_A}{dt} = -\frac{dC_E}{dt} \\ &\mathrm{GL}: \frac{dC_{GL}}{dt} = k_5C_{\mathrm{MG}}C_A - k_6C_{\mathrm{GL}}C_E + k_7C_{\mathrm{TG}}{C_A}^3 - k_8C_{\mathrm{GL}}{C_E}^3 \end{aligned} \tag{3}$$

Eq. (3) together with the experimental data was used in simulation studies to obtain the values of reaction rate constant.

3.3. Biodiesel reactors

Various types of reactors have been used in biodiesel production plants. Among them are batch and continuous reactors, the latter can be either a CSTR or a plug flow reactor. Processing biodiesel in batch system was employed by Sakai et al. [40] using homogeneous and heterogeneous alkali-catalysed processes for a biodiesel production from waste cooking oil ranging from 1452 t/year (5000 l/day) to 14,520 t/year (50,000 l/day). They selected KOH as a homogeneous catalyst and CaO as a heterogeneous catalyst and evaluated the cost of both. In addition, a batch reactor was also used in biodiesel production using supercritical alcohol [41].

On the other hand, continuous reactors were also used in biodiesel production [42,43]. Avellaneda et al. [44] compared continuous reaction with batch reaction for biodiesel production from waste cooking oil. For continuous production, they employed helicoidal type of reactor which comprised of a series of spirals of length *L*, each connected consecutively by a fixture with four exits. This fixture enabled each spiral to be assembled with the next one, and to connect a valve for taking samples of the internal fluid and a thermocouple for measuring temperature. For comparison, the biodiesel obtained through the helicoidal reactor was very similar to that obtained in the batch process under the recommended conditions, but the reaction time was substantially lower.

Besides the aforementioned studies, some research also included the use of membrane reactors [45], bubble column reactors [38], zigzag micro-channel reactors [46], jet flow stirred reactors [47] and packed bed reactors [48–50] to produce biodiesel. The following table shows the comparisons of biodiesel fuel production using different types of current reactors Table 1.

In reviewing current reactors for biodiesel fuel production, most of the reactors are capable of delivering maximum purity of biodiesel fuel within the specified conditions. Among the current reactor being compared, membrane reactors offer methanolysis that do not require downstream processes. It should be noted that the reactors used are on a laboratory scale and still in the research stage. A further study with more focus on kinetic analysis, costs analysis and study of control system are therefore recommended for industrial biodiesel fuel production.

4. Process simulation

Process simulation studies offer convenient tools for determining process characteristics and their dependence on design and operating variables [33]. Process simulations usually begin with the determination of the chemical components, and selection of suitable thermodynamic model. Subsequently, unit operations, operating conditions, input conditions and plant capacity must be specified. Most of the property data of components are available in the software library. However, if certain component property is unavailable in the simulator library, registration of the component can be made by introducing the component as a new chemical component.

García et al. [51] conducted a simulation study to predict normalized biodiesel properties using different feedstock. They compared the results with previous experimental data in terms of thermodynamic packages used. They found that the predictive model was mostly well-suited to experimental data. At variance to García et al., Zhang et al. [25] conducted simulation of biodiesel plant from waste cooking oil using different types of catalysts. They employed alkali-catalysed transesterification and acid-catalysed transesterification of biodiesel. As mentioned earlier, designs of biodiesel plants were carried out, and then simulated using available thermodynamic models. The simulation showed that for an alkali-transesterification process using pure oil to produce biodiesel, the right amount of water could lead to near complete separation between the FAME and glycerol phase. Acid-catalysed transesterification reaction conducted by Zhang et al. applied higher reaction temperature, pressure, and higher methanol to oil molar ratio than alkali-catalysed transesterification. In addition, acid removal process was also employed.

Similar to simulation studies conducted by Zhang et al., a process simulation was also carried out by Sotoft et al. [52] for biodiesel production using enzymes as the catalyst. Comparison was made between the processes with the existence or absence of co-solvents. In their study, Sotoft et al. utilized 3 CSTRs in series with the reactors and simulation made using Aspen Plus computer simulator. The findings showed promising yield of solvent free enzyme biodiesel production. In contrast, Kaewcharoensombat et al. [53] performed process simulations of biodiesel from

Table 1
Comparisons of biodiesel fuel production using different types of reactor.

References	Reactor type	Features	Reaction conditions	Advantages of reactor
[45]	Membrane reactor	Volume: 300 mL Equipped with carbon membrane, pump and heat exchanger. Membrane pore size: 0.05 μm Membrane inside diameter: 6 mm Membrane outside diameter: 8 mm Membrane length: 120 mm Membrane surface area: 0.022 m^2 Pressure: 138 kPa	Feedstock: Canola oil Temperature: 60–70 °C Reaction time: 6 h Catalyst: 0.5–6 wt % sulfuric acid	Provide simplification for FAME purification processes. Provide a phase barrier to limits the presence of TG and unreacted lipids in the end product
[38]	Bubble column reactor	Volume: 500 mL Equipped with condenser molecular sieves, pump, tin bath, and methanol dehydrating column.	Feedstock: refined palm oil Temperature: 523–563 K Superheated methanol pressure: 0.1 MPa Superheated methanol temperature: 503–533 K Superheated methanol feed rate: 4 g/min	Accomodate superheated methanolysis process
[47]	Jet flow stirred reactor	Volume: 9000 mL Equipped with pumps and heating unit	Feedstock: blend of soybean oil and sunflower oil Temperature: 90 °C Reaction time: 1 hour Catalyst: 1 wt %	Offer dual jet flow injection with flow circulation
[48]	Packed bed reactor	Volume: 196 mL Equipped with peristaltic pump, TYGON tube glass column packed with cuboid PU biomass support particles containing dry *R. Oryzae* cell.	Feedstock: soybean oil Temperature: room Ultrasonification process included.	Offer repeated-batch methanolysis with whole-cell biocatalyst

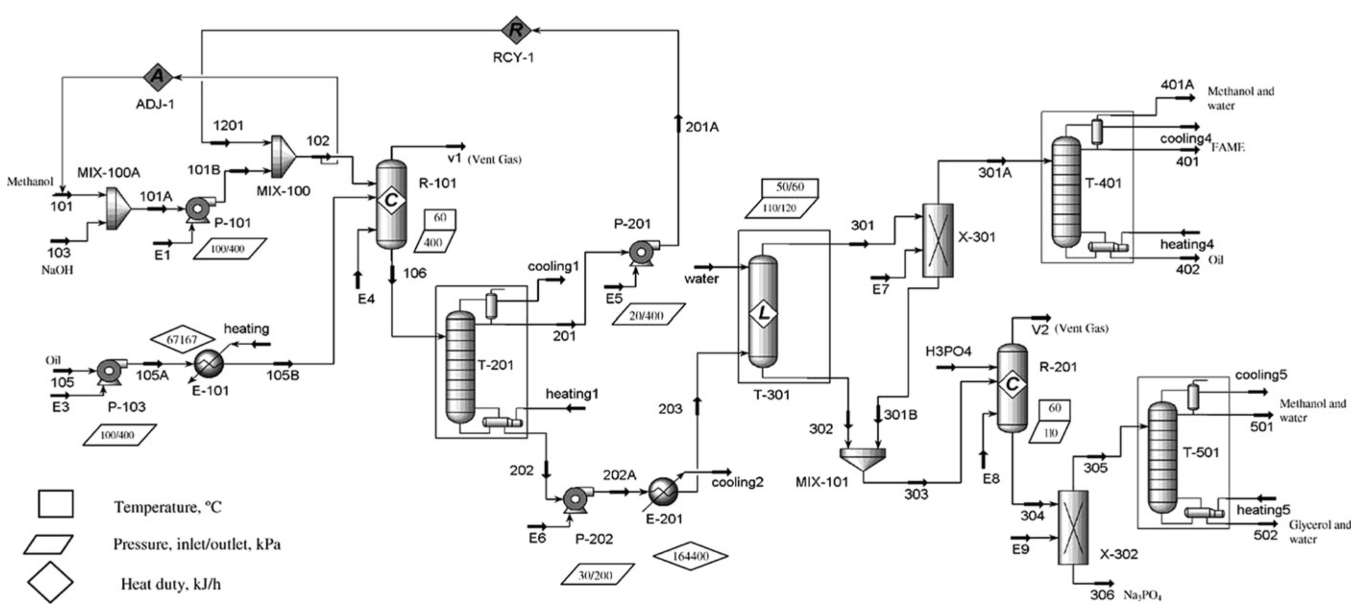


Fig. 5. Flow sheet of biodiesel plant design by alkali-catalysed transesterification of virgin oil.

various feedstock. They used waste cooking oil, rapeseed oil and Jatropha oil as feedstock in the alkali-catalysed transesterification reaction. They could obtain high purity biodiesel when the process is simulated using Aspen Plus process simulator.

West et al. [54] performed simulation on biodiesel processes using various types of catalysts, which also included simulation on a supercritical process. They employed the HYSYS process simulator, and found that all the simulated processes were capable of achieving ASTM grade biodiesel. Figs. 5–7 show the process flow diagrams of simulated biodiesel fuel production carried out by Zhang et al., Sotoft et al. and West et al.

According to the above process flow diagrams, the main process units are reactors, distillation columns, heat exchanger, washing column, pumps and storage tanks. Although the process units mentioned could be found in each process flow diagram, the processes of biodiesel fuel production could differ depending on

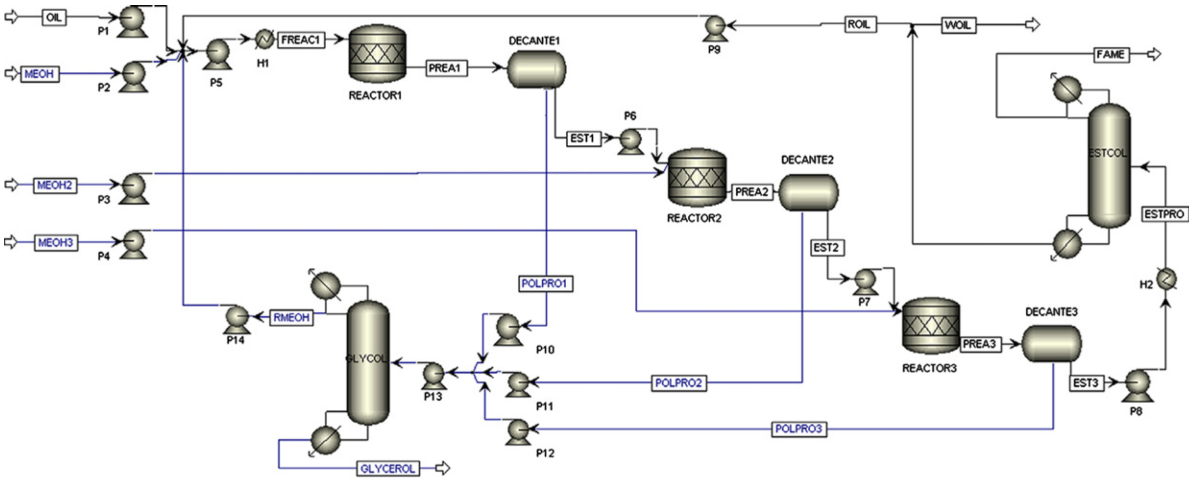


Fig. 6. Flow sheet of biodiesel plant design by enzyme-catalysed transesterification of rapeseed oil.

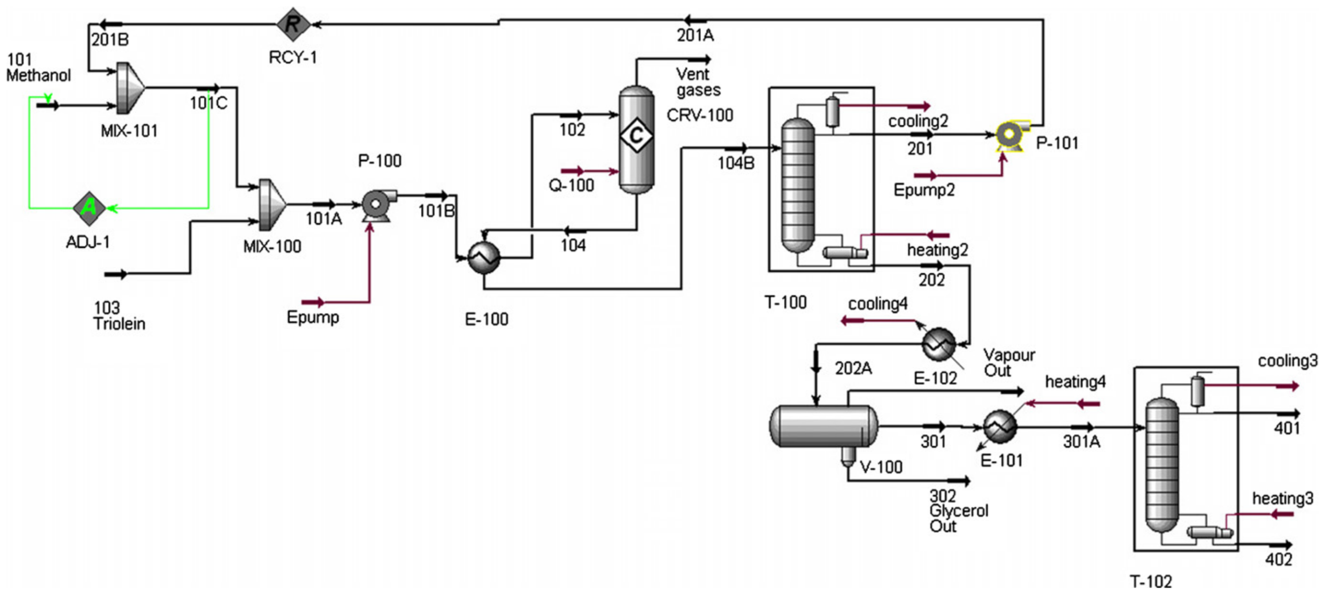


Fig. 7. Flow sheet of supercritical alcohol plant design.

the absence or presence of catalyst, purity and type of feedstock. Nevertheless, all the simulations carried out within the specified operating conditions have proven that all process flow diagrams are capable of producing high quality biodiesel within the specified operating conditions. However, each process has a number of limitations. For example, both the alkali-catalysed transesterification using virgin oil and the enzyme-catalysed transesterification requires costly raw material or expensive enzymes. On the other hand, the supercritical alcohol process requires high-pressure reactors and large amounts of energy to separate the methanol from the feed stream, thus increasing the total costs.

Simulation studies are usually accompanied with production cost estimation and impact on the environment. The simulation studies conducted by Haas et al. [55] focused on developing a model for estimating the cost of biodiesel production using soybean oils as feedstock. The process consisted of transesterification, methyl ester purification and glycerol recovery sections. Capital and production costs were also estimated. It could be inferred that the costs calculated were suitable for biodiesel derived from soybean oils, but not applicable for biodiesel from other feedstock, as additional processes may be required depending on the oil characteristics. Jegannathan et al. [56] examined the cost of biodiesel production of different types of catalysts. Costs were compared between the alkali-catalysed and enzymatic-catalysed processes, which are either soluble or enzyme-immobilized. At variance to Haas et al., Jegannathan et al. also performed batch operations of biodiesel. They discovered that the cost of alkali-catalysed process was lower compared to enzymatic-catalysed process. They also suggested that, if the immobilized catalyst could be repeatedly reused, its production cost could beat the alkali-catalysed production cost. Similar work was conducted by Sakai et al. [40] but they included investigation of different types of process plants and manufacturing cost.

Other economic viability study was conducted by Araujo et al. [57] for an assessment of biodiesel production cost of waste frying oil. They extended the scope of estimation cost when they also evaluated the logistic cost of obtaining waste frying oil from certain places such as restaurants. An estimation cost study of biodiesel produced in supercritical process by Deshpande et al. [22] indicated that the highest cost was incurred on raw materials and labour. If comparison of cost was made on different types of feedstock used,

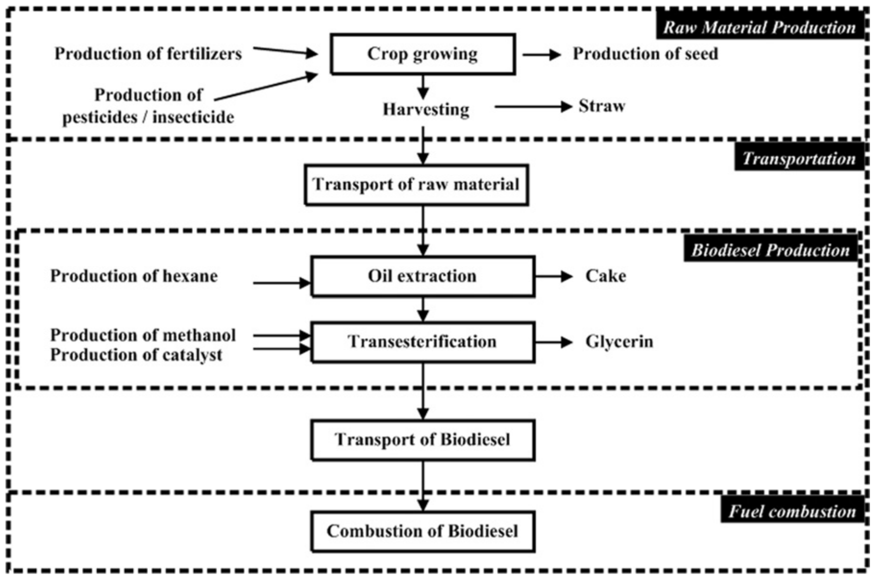


Fig. 8. Life cycle inventory of biodiesel.

biodiesel derived from canola oil would be found less costly compared to other types of feedstock such as soybean oil [58].

5. Process optimization

Process optimization of biodiesel production is essential for determining the values of important variables to achieve the highest performance criteria. In plant operations, benefits did arise from improved plant performance, reduced energy consumptions, reduced maintenance cost, less equipment wear and better staff utilization [59]. To reap the benefits, critical analysis of the process or design, accomplishment of specific targets, and use of experience is required.

Optimization of biodiesel plant also depends on types of systems applied. Optimization often concerns minimization of cost and maximization of economic potential (EP) known as objective function. For example, heat integration and cost of the heat exchanger network and utilities have significant influence on the optimum conversion. Also, if there are two separators, the order of separator system can influence the reactor conversion.

At the design stage, optimization process depends on the variables involved in the process itself. For example, once the objective function has been determined; for a single variable, it involves a one-dimensional search. Methods for single-variable search are region elimination and Newton's method. Search method used for multivariable optimization can be classified as deterministic and stochastic. Deterministic can be either direct or indirect search methods; and stochastic can be either simulated annealing or genetic algorithm. Most optimization problems involved constraints which include three basic elements such as objective function, equality and equality constraints. If all elements are linear, search methods for such problems are developed in linear programming. But if the objective function, equality or inequality constraints are nonlinear, the optimization becomes a nonlinear programming problem [24].

Recently, other than economic issues, optimization in PSE also concerns the environmental issues in the synthesis and planning of chemical process. A systematic method was introduced by Ignacio and Gonzalo [60] on how to reach optimal environmental conditions and maximize the profit. Generally, the techniques can be observed under three sections; process synthesis, supply chain management, and impact assessment method. In process synthesis, alternatives of process are first listed, followed by selecting the optimum processes. Subsequently, mathematical programing is formulated followed by solutions for the optimization problem using mixed integer linear programming, mixed integer non-linear programming; or any suitable method to find the optimal.

An optimization study on process synthesis was conducted by Di Nicola et al. [61] using modeling and multi-objective genetic algorithm optimization in biodiesel production processes. The study was to determine the configuration of main parameters to obtain maximum purity of some important compounds, and for minimizing the energy requirements in the process. In contrast to Di Nicola et al., Halim et al. [62] focused on optimization of acid-catalysed process using waste canola oil for minimizing the waste of biodiesel synthesis, and maximizing the profit. They employed multi-objective simulated annealing algorithm. The methods were proven to enhance both the impact and profit of glycerol as a waste by-product.

Optimization of supply chain management (SCM) is often performed to find optimal investment solutions. For biodiesel production, SCM is conducted at an earlier stage of production process via the analysis of conditions required to fulfil the demand of oil feedstock for biodiesel plant. Leao et al. [63] optimized the structure for supplying oil to biodiesel plant by developing mathematical programming and identifying optimal conditions using computer simulation. The factors considered were production, transportation and crushing of oil seeds and transportation of oil to the biodiesel plant. On the other hand, Leduc et al. [64] conducted optimization to find optimal location for Jatropha biodiesel plant. Similarly, mathematical programming was conducted and analysed using various feedstock. Besides that, Srinivasan and Malliga [65] conducted optimization of Jatropha seed yielded at a cultivable wasteland. The optimization was made using corporate fuzzy inference system, involving factors that influenced the Jatropha yield such as irrigation, fertilizer usage, rainfall, temperature, acidity and altitude. Interestingly, optimization is performed in supply chain management as a strategy for customer satisfaction starting from raw material the end-consumer spectrum.

Meanwhile, in order to evaluate the environmental impact, optimization is based on life cycle assessment (LCA). Kaewcharoensombat et al. reported that the LCA was performed after process simulation to determine the environmental impact [53].

As shown in Fig. 8, the life cycle of biodiesel starts with raw material production, transportation, biodiesel production and finally fuel composition. Damage analysis was focused on three categories, i.e., resources, human health and ecosystem quality. They found that biodiesel production stage contributed to higher environmental impact compared to other stages. Concerns of the GHG emission compelled Choo et al. [66] to conduct the LCA of biodiesel from palm oil. The LCA inventory included nursery, plantation, palm oil mill, refinery, and biodiesel plant. At each stage, analysis was carried out to determine the amount of GHG emissions that it produced. The results showed that GHG emissions occurred during the milling process from the use of fertilizer. Evidently, optimization is an excellent strategy that offers promising solutions for desirable conditions either in maximizing profit, minimizing waste or reducing environmental impact.

6. Integration of reactor system and separation system

Simultaneous reaction and separation process in biodiesel processing can be created using reactive distillation and membrane separation technique. This type of integration combines the reaction and separation into one unit by incorporating either mass or heat in the synthesis process. They offer benefits such as simpler unit operation, waste-free and improve both economic and environmental performance [67–69]. However, in process system engineering, integration of reactor and separation system is enabled through a synthesis of reactor–separator-recycle system. It consists of combining the reactor network with separation network that includes superstructure modeling such as MINLP; and solving the MINLP issues to provide information on optimal configuration of the system [70]. A drawback is that very limited number of publications on optimization of reactor–separator-recycle systems in biodiesel synthesis are currently available.

7. Suggestion for future works

For future work, it is suggested that application of mathematical programming techniques in the synthesis and planning of sustainable biodiesel process should be attempted. The work may focus on establishing environmental improvements through process synthesis and supply chain management by employing mixed-integer optimization, multi objective optimization and uncertainty methods [60]. Apart from using mathematical programming techniques, the use of heat integration in the optimization of biodiesel production processes can also lead to minimizing the operating cost [71,72]. It can be implemented by modeling mixed integer nonlinear problem (MINLP) involving mass and energy balances for all the units in the system; followed by optimizing the processes with respect to energy consumption [73,74]. Another suggestion is the development of superstructures of biodiesel production processes that include heat integration and non-heat integration; and comparing the superstructures sustainability. Superstructure with sustainable alternatives or features may then be considered as functions of economy and energy as both are related to profit [73]. Heat integration can also be conducted along with mass integration synthesis for waste minimization [75,76].

8. Conclusion

Recent gains in the development of biodiesel fuel production have been reviewed and discussed. It is clear that a lot of research and study have been carried out, especially in developing new more active catalysts that are capable of increasing biodiesel purity as well as helping to speed up the process of biodiesel production. Research should be more focused on the development of super active and robust catalysts. Apart from that, both esterification and transesterification reactions may become more efficient using reactive distillation when a super active and robust catalyst is available [77]. This helps to reduce capital and investment costs and may be beneficial for sustainable development due to the lower consumption of resources. In addition, kinetic studies of new processes in biodiesel fuel production are currently being pursued. Furthermore, flow sheeting and simulation studies in biodiesel fuel production have shown the importance of obtaining the best operating conditions and verifying experimental results. The availability of powerful process simulators has enabled process engineers to cope with the complex problems of designing processes to produce the highest biodiesel purity. This review has shown that there are numerous alternative processing methods and process units in producing biodiesel fuel. Process optimization using reactor-separation-network (RSN) has provided an opportunity to acquire an optimum solution apart from obtaining the lowest production costs during the process selection stage. This review has shown that process system engineering is an excellent approach to systematically design and operate the complex biodiesel production system. Integrated models, methodologies and tools need to be developed through process model and design, simulation, optimization, experimentation and visualization. Yet, integrating any combination of tools into the PSE approach is quite challenging since interaction among system components is yet to be fully understood. Therefore, the application of computer aided PSE tools for the synthesis, design, control and modelling of the biodiesel process can further advance the frontier of knowledge in this field.

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